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Final Report

## CHEMICAL ORIGIN OF THE VENUSIAN CLOUDS

By: ROBERT C. ROBBINS

Prepared for:

OFFICE OF RESEARCH GRANTS AND CONTRACTS  
CODE S.C.  
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION  
WASHINGTON, D. C. 20546

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*Approved:*

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SRI-Irvine

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## INTRODUCTION

The objective of this study was the laboratory investigation of chemical reactions between components believed to be present in the upper atmosphere of Venus that might ultimately produce cloud components in the form of condensed organic polymers.<sup>1</sup>

During the Mariner II Venus fly-by in 1962, the magnetometer failed to detect any magnetic field on Venus,<sup>2</sup> which was considered to be evidence for a slow rotation rate of the planet.\* We expected this absence to allow the solar wind to impinge directly on the atmosphere of Venus. The solar wind then would be the source of excited hydrogen atoms in our theory of organic cloud formation. Mariner II measured the particle flux of the solar wind to be about  $10^9$  protons  $\text{cm}^{-2} \text{sec}^{-1}$  from a quiet sun.<sup>3</sup> The levels measured by Mariner II were in agreement with earlier values from Lunik II, Lunik III, and Explorer X.

Radar measurements also indicated that the rotation rate of Venus is slow and retrograde.<sup>4</sup> Pettengill at Arecibo, Puerto Rico,<sup>5</sup> estimated a rotation rate of  $253 \pm 5$  days. With a retrograde rotational period of 253 days, the sun will rise once every 119 earth days. Thus, the sunlit period is about 1400 hours and it is followed by 1400 hours of darkness. This relatively long dark period could have provided the necessary conditions to allow extensive polymerization reactions to occur in the absence of photolytic effects. If organic polymers were present at sunset,

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\* This assumption is made on the basis that the most plausible theory concerning the cause of the Earth's magnetic field is that a dynamo effect is produced in the core due to the rapid rotation.

the long night would give the droplets time to sink to lower atmospheric levels where they would be protected from photolysis. At 30 to 100 km, many of the condensed organic compounds might be stable.

The analysis of the Mariner V and Venera 4 data and recent spectroscopic data have added a large amount of new and better information concerning the composition and structure of the Venus atmosphere. It is now obvious that our first atmospheric reaction model was incorrect. The best model available at the present time has low concentrations of water vapor diffusing upward from the surface<sup>6</sup> instead of solar protons penetrating the atmosphere from above.

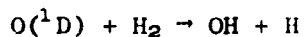
Before the Mariner V fly-by of Venus, the existence of a bow shock around the planet was not suspected. Data from this probe clearly showed the existence of a magnetohydrodynamic shock, which must be caused by interaction between the solar wind and the ionosphere of Venus. The Venus bow shock diverts the solar wind and effectively shields the atmosphere of Venus, preventing the entry of solar hydrogen.<sup>7</sup> While the data from Mariner V virtually prove that the solar wind cannot be a source of hydrogen in the Venus atmosphere, as was assumed for our first model, ultraviolet photometer experiments made from this probe indicate that there is hydrogen in the atmosphere of Venus.

Barth<sup>8</sup> and McElroy and Hunter<sup>9</sup> have worked over the Lyman alpha emission data from Mariner V. They agreed that Lyman alpha emissions implied a net flow of hydrogen escaping from the atmosphere. Both the McElroy-Hunter model and the Barth models call for low concentrations of hydrogen in the atmosphere of Venus.

The observed absence of CO<sub>2</sub> dissociation products in the high Venus atmosphere is also significant.<sup>10</sup> It appears that the CO<sub>2</sub> atmosphere is much more stable than was expected; this stability may be explained by the assumption of a very fast recombination mechanism. Even though the



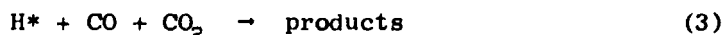
water vapor concentration is small, Belton<sup>11</sup> calculated the ratio of H<sub>2</sub>O/CO<sub>2</sub> to be 10<sup>-4</sup> at the cloud top; this amount of water at the dissociation level should provide enough OH to convert CO rapidly back to CO<sub>2</sub>. Excited oxygen O(<sup>1</sup>D) reacts rapidly with H<sub>2</sub><sup>12</sup>



but postulating an adequate supply of H<sub>2</sub> molecules for this reaction is difficult. Whatever the mechanism, very low concentrations of CO, O, and O<sub>2</sub> are found in the upper atmosphere of Venus.

## EXPERIMENTS AND RESULTS

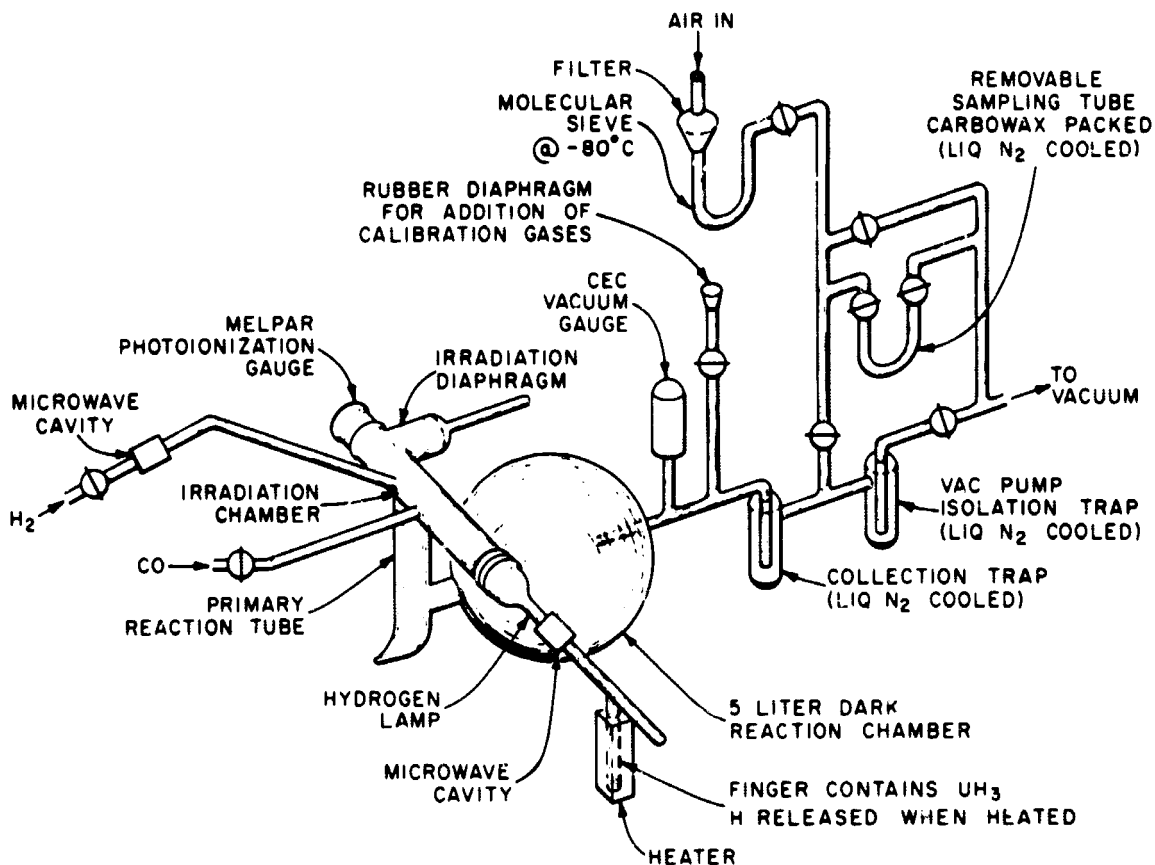
Excited atomic hydrogen was used to simulate partially thermalized and neutralized solar protons from the solar winds that were expected in the high atmosphere of Venus. First studied were the primary reactions of excited atomic hydrogen with components that were expected in the high atmosphere of Venus:



The reactions were studied in a flow system in which ground-state hydrogen atoms were irradiated with Lyman- $\alpha$  and then mixed with the reactant(s). After the gas mixture passed through a dark reaction chamber, the condensable products were collected in a cold trap. The collected material was analyzed by gas chromatography equipment. The first arrangement used is shown in Fig. 1.

Reaction (1) between excited hydrogen atoms and carbon monoxide yields intermediate radical species and atom species that undergo rapid secondary reactions to produce water and organic compounds. The principal organic compounds formed are ethylene, formaldehyde, and glyoxal, all readily polymerizable substances.

A detailed qualitative and quantitative analysis of the products was made. On a mole basis, the products were 70% water and 30% organic compounds. The chromatograph showed 13 organic peaks of which five were



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FIGURE 1 FIRST EXPERIMENTAL ARRANGEMENT

positively identified, four tentatively identified, and four unknown. Half of the organic product was ethylene; two other major organic components were formaldehyde and glyoxal. In addition, methanol, ethane, acetylene, propylene, acetaldehyde, acetone, ethanol, and formic acid were tentatively identified as being present.

Water was measured in the following manner: the product gases were passed through a calcium carbide cartridge heated to 160°C, and the acetylene formed was measured by the flame-ionization detector.

A comparison of the water/organic product ratio (70/30) with the heats of reaction ( $\Delta H$ ) of the two reactions,



is of interest. Reaction (6) is the water-producing reaction; it is exothermic by 75 kcal/mole. Reaction (7) is the organic-producing reaction; it is exothermic by 60 kcal/mole.

In view of the nature and distribution of the products, the two second-stage reactions that are probably most important are



Reaction (2),  $\text{H}^* + \text{CO}_2 \rightarrow \text{products}$ , could possibly produce some CH, i.e.,



instead of the more probable



When reaction (2) was investigated experimentally, no organic products were found. Thus, reaction (10) is of little importance, and the OH produced reacts with  $\text{H}_2$  and CO as follows:



In the high atmosphere of Venus, there is no large excess of  $\text{H}_2$  in contrast to the laboratory conditions. Therefore, reaction (8) has no significance, and the reaction route is defined by reaction (12). A less important recombination reaction also occurs,



When  $\text{CO}_2$  is added to the  $\text{H}^* +$  system, reaction (3), the water/organic product ratio is increased via reaction (11). One part  $\text{CO}_2$  per ten thousand CO caused a 20 to 30 percent reduction in the organic yield. On the other hand, when nitrogen is added to the  $\text{H}^* + \text{CO}$  system, reaction (4), organic compounds are produced, even though nitrogen is not a component of the organic products. When both  $\text{CO}_2$  and  $\text{N}_2$  are added to the  $\text{H}^* + \text{CO}$  system, reaction (5), the  $\text{CO}_2$  inhibiting effect strongly overrides the  $\text{N}_2$  enhancement effect on the production of organics.

The irradiation chamber was designed for maximum production of excited hydrogen atoms and the reaction tube with its CO inlet line was designed to provide optimum mixing conditions of  $\text{H}(^2\text{P})$  and CO. Production rates of  $10^{14}$  to  $10^{15}$  molecules  $\text{sec}^{-1}$  were obtained. From this measured production rate a minimum rate coefficient of  $10^{-15}$  cc molecules $^{-1}$   $\text{sec}^{-1}$  was estimated, but the actual rate coefficient is almost certainly larger.

The measurement of H atom concentration was attempted using a Melpar photoionization detector designed by NASA in 1959. Equipped with a thin LiF window, it was filled with 20 torr pressure of NO and had a spectral response range of 1050 to 1350 Å and a quantum efficiency of 30%. The guard ring was at ground potential and the shell electrodes at 45 V. The photoionization current was fed into a recording Varian micromicroammeter. Photoionization current measurements failed to show  $\text{H}(^2\text{P})$  production due to strong line broadening of the radiation from the hydrogen lamp.

In the early experiments, the total pressure in the flow system was maintained at 2 torr and the relative flow rates of the  $\text{H}_2$  and the CO were varied between 1  $\text{H}_2/1$  CO and 100  $\text{H}_2/1$  CO.

The hydrogen used was purified by passing through a palladium-silver alloy thimble. The CO was passed through magnesium perchlorate to remove water vapor and oxygenated hydrocarbons, then through ascarite to remove CO<sub>2</sub>. Small amounts of methane and ethane were the only impurities remaining in the CO.

The hydrogen lamps used contained uranium hydride. The hydrogen pressure and the irradiation intensity were controlled by controlling the temperature of a well containing the uranium hydride. The uranium in these lamps served the dual purpose of supplying the hydrogen and of continuously reacting with and removing any foreign gases which might appear in the gas phase by desorption from the walls. Both lithium fluoride (LiF) and magnesium fluoride (MgF<sub>2</sub>) windows were used. While the Lyman- $\alpha$  transmission of the LiF windows slowly decreased with use, the MgF<sub>2</sub> did not appear to be affected by the radiation from the hydrogen lamp.

The flow rate through the system was 250 cc sec<sup>-1</sup> at 2 torr pressure. Thus the residence time in the 50-cc irradiation chamber was 0.2 sec and the residence time in the 5-liter dark reaction chamber was 20 sec. After leaving the dark reaction chamber, the product mixture passed into a trap cooled with liquid nitrogen where all of the reaction products were condensed and collected. Following the reaction period, which was generally 15 minutes, the collected products were transferred to a small copper loop trap, packed with Carbowax supported on firebrick. The transfer was made by cooling the copper loop with liquid nitrogen, warming the collection trap with hot water, and carrying the products in hydrogen gas with about 100 torr pressure drop across the copper loop. Fifteen minutes were required for the transfer. Then the liquid nitrogen-cooled loop was removed from the system and carried to a flame-ionization detector, where the loop was connected into the carrier gas stream and the sample analyzed.

Two analytical procedures were used for organic components: in the first procedure, the sample was carried directly into the flame ionization detector from the loop trap with no chromatographic column; in the second procedure, a 6-ft Carbowax column was added to enhance component resolution.

The optimum experimental procedure was to make 15-min runs with selected H<sub>2</sub> and CO flow rates, followed by 15-min transfers to the sample loop, and then to analyze the collected products using the flame ionization detector.

System blanks were obtained by making complete 15-min runs and 15-min collections with all experimental conditions identical to the conditions of a reaction experiment except that no excited species were present. These system blanks were checked carefully for reproducibility. Blank runs were made immediately before and after reaction runs, and this three-part sequence was repeated several times under each set of operating conditions.

Analysis of the blank run chromatograms showed that the background spectrum of components was reproducible. While there were five small peaks, the variation in peak height from blank to blank was less than 20%. Comparison of the blank run chromatograms with reaction run chromatograms showed that all of the methane and part of the ethane were impurities in the CO reactant. Based on quantitative analysis of water vapor (acetylene), the concentration of methane in the CO was calculated to be 50 ppm.

Two definitive experiments were made to confirm the assumption that ground state H atoms do not react with CO. In the first, a 15-min blank run was made with ground state H atoms being produced by the microwave unit for that purpose. Analysis of the collected sample was essentially identical with the analysis of the normal blank runs. In a second 15-min

run with ground state H atoms, the condensible components were collected with the trap cooled by liquid oxygen (to prevent condensation of CO). When the collection trap was warmed, the pressure increase in the isolated system was 2 microns. This increase was attributed to the methane and ethane.

Between the extremes of flow ratios of H<sub>2</sub> and CO used, twice as much product was formed at 100 H<sub>2</sub>/1 CO (2 torr H<sub>2</sub>/20 micron CO) as at 1 H<sub>2</sub>/1 CO (1 torr H<sub>2</sub>/1 torr CO). However, even at 100 H<sub>2</sub>/1 CO the ratio of H(<sup>2</sup>P) to CO was probably about 1[H(<sup>2</sup>P)]/100 CO, so the amounts of product formed were proportional to the H(<sup>2</sup>P) concentrations.

When the sample was added directly to the flame-ionization detector, it was allowed to warm up slowly by simply removing the loop from liquid nitrogen. This produced a quite reproducible "temperature-programmed" series of component peaks. Seven separate peaks appeared as the temperature rose to room temperature, and two more were seen when the trap was heated with boiling water.

Several of the peaks were easily identified. The first four, completely separated, were methane, ethane, ethylene, and acetylene. The next three peaks were possibly combinations of components. For example, formaldehyde and acetaldehyde came out together. The last two "hot water" peaks were apparently a mixture of methanol, ethanol, formic acid, and acetic acid.

From the organic component analysis by direct injection of the sample into the flame-ionization detector, the relative importance of ethylene, formaldehyde, and glyoxal production by the H(<sup>2</sup>P) + CO reaction was shown.

The analytical system was calibrated by quantitatively determining the water produced by the reaction. Using the same basic experimental and analytical procedure described earlier, the apparatus was modified by adding a calcium carbide (CaC<sub>2</sub>) cartridge between the sample transfer



valve and the sample loop. Calcium carbide produces a molecule of acetylene for every two molecules of water reacted. It was necessary to condition the glass surfaces of the apparatus by adding an adsorbed monolayer of water molecules (about 10  $\mu$  moles) before reproducible amounts of water vapor could be transferred from the apparatus into the sampling section. Operation of the  $\text{CaC}_2$  cartridge at room temperature gave non-reproducible acetylene measurements due to the absorption of water vapor on the  $\text{CaC}_2$  and the calcium hydroxide  $[\text{Ca}(\text{OH})_2]$  reaction product. When the  $\text{CaC}_2$  cartridge was heated and operated at 160°C, the material in the cartridge was maintained in an anhydrous condition and the analytical method became reproducible and quantitative. The system was calibrated by adding known amounts of water vapor (1 to 2  $\mu$  mole increments) and determining the amount of acetylene produced. The intrinsic sensitivity of this method of water analysis is  $10^{-10}$  moles.

Several 15-min reaction runs were made; Table I shows the results of water determination of four successive experiments under the same nominal conditions (1  $\text{H}_2$ /1 CO pressure). The continuous decrease in water production probably reflects a decreasing transmittance of Lyman- $\alpha$  by the LiF windows with a corresponding decrease in  $\text{H}(^2\text{P})$  atom concentration.

Table I

WATER PRODUCTION

Run No.	$\mu$ Moles
1	0.80
2	0.78
3	0.55
4	0.38

Av 0.63  $\pm$  0.18  $\mu$  moles  
water for 15-min run

After the water production was quantitatively determined, the organic components were qualitatively and quantitatively determined with a 6-ft Carbowax column added to the flame ionization detector system and peak areas referred to the known acetylene peak area, which was calibrated against water. The elution times of all of the expected CH and CHO compounds were determined for the 6-ft Carbowax column with the column operating at 100°C. Elution times were determined for methane, ethane, ethylene, acetylene, propylene, formaldehyde, acetaldehyde, ethylene oxide, glyoxal, acetone, methanol, and ethanol.

The total organic fraction was about 30 mole %, water accounting for the 70 mole %. The amounts of reaction products are given in Table II. As previously mentioned, methane and ethane were major components of blank runs, and these are not listed as reaction products. In addition to compounds listed in Table II, those positively identified as being present in the 3% were ethane and acetylene. Compounds possibly present included propylene, acetaldehyde, acetone, ethanol, and formic acid.

Table II

REACTION PRODUCTS

Compound	Mole %
Water	70
Ethylene	15
Glyoxal	5
Formaldehyde	5
Methanol	2
Other Organics	3

Of thirteen peaks (excluding methane) exhibited by the chromatographs, five were fully identified as single components, four were not fully resolved and might have consisted of two or more of the oxygenated compounds, and four peaks were not identified.

The reaction system was modified by replacing the 5200 ml dark reaction sphere with a small (5 ml) irradiation chamber and a small cold finger directly downstream of the irradiation chamber. A mercury lamp was used for the secondary irradiation.

With the original cold trap remaining in place, two reaction volumes were provided. The reaction volume to the first trap was 125 cc, giving a 0.50 sec reaction time at 2 torr pressure. The reaction volume of the second trap was 43 cc, giving a 0.17 sec reaction time.

Fifteen min reaction runs were made, again using 1 torr H<sub>2</sub> and 1 torr CO. Product collections were made under three conditions:

1. 0.5 sec reaction time
2. 0.5 sec reaction time with secondary irradiation by the mercury lamp
3. 0.17 sec reaction time.

The product distribution was somewhat different under the new conditions; the kinds and amounts of product are given in Table III. The product decrease with secondary photolysis is quite pronounced and quite variable among the compounds. Analysis of the reaction product data at times of 0.17 and 0.50 sec shows that about 10% of the CH + OH is reacted in 0.05 sec. The H(<sup>2</sup>P) half-life is 0.02 sec. The radiative lifetime of H(<sup>2</sup>P) is  $1.2 \times 10^{-8}$  sec, and the population of excited atoms is maintained by imprisonment of the resonance radiation due to the high concentration and production rate of H(<sup>2</sup>P). From the half-life and the initial concentration, the rate constant for reactions (6) and (7) combined was

Table III

MICROMOLES OF PRODUCTS FORMED IN TWO REACTION TIMES  
AND EFFECT OF SECONDARY IRRADIATION ON YIELDS

Reaction Time	H <sub>2</sub> O	HCHO	(CHO) <sub>2</sub>	CH <sub>2</sub> =OH <sub>2</sub>	CH=CH	HCOOH	CH <sub>3</sub> CHO	CH <sub>3</sub> OH	CH <sub>3</sub> COCH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub> OH
0.5 sec	0.90	0.130	0.070	0.052	0.043	0.040	0.032	0.009	0.008	0.007
0.5 sec with irradiation (photolysis)	nm	0.088	0.035	0.043	0.024	nm	0.014	0.001	0.006	nm
0.17 sec	0.15	0.020	0.010	0.002	0.002	nm	0.000	0.000	0.003	nm

nm = not measured.

calculated to be approximately  $10^{-11}$  cc molecules<sup>-1</sup> sec<sup>-1</sup> at 300°K. The secondary recombination reactions producing stable compounds at an initial CH + OH concentration of  $10^{12}$  molecules/cc occur at such a rate that the radical half-life is 0.15 sec. The quantitative relationships are presented in Fig. 2.

Again, an approximate rate constant can be calculated for organic compound formation from reactions of the CH radical. This calculated rate constant at 300°K is  $2 \times 10^{-12}$  cc molecules<sup>-1</sup> sec<sup>-1</sup>, 5 times slower than the H(<sup>2</sup>P) + CO reaction. The individual production rates of organic compounds are proportional to the relative amounts produced.

A few experiments were made using CO + N<sub>2</sub> + H(<sup>2</sup>P), but the brass bellows valve in the sample transfer system removed all of the NH<sub>3</sub> and amines produced. As the organonitrogen compounds were of little interest, no other reactions that included nitrogen in the reaction mixture were studied.

After this phase of the work was finished, it was decided that it was necessary to investigate reactions of H<sub>2</sub> with CO, CO<sub>2</sub>, and mixtures of CO<sub>2</sub> and CO on the possibility of there being a surface source of H<sub>2</sub> on Venus.

A large number of experiments were then performed in the vacuum system after extensive modification for maximum flexibility. The revised system incorporated a supply manifold through which H<sub>2</sub>-CO, H<sub>2</sub>-CO<sub>2</sub>, or H<sub>2</sub>-CO-CO<sub>2</sub> mixtures could be added in various combinations and at known flow rates.

Small loop traps of copper tubing, with Swagelok fittings and packed with Chromosorb, were added to the reaction system, and a chromatographic column plus flame ionization detector was coupled directly to the vacuum system. A hydrogenation furnace placed ahead of the flame ionization detector was optional for improved formaldehyde and formic acid analysis and to detect carbon suboxide.

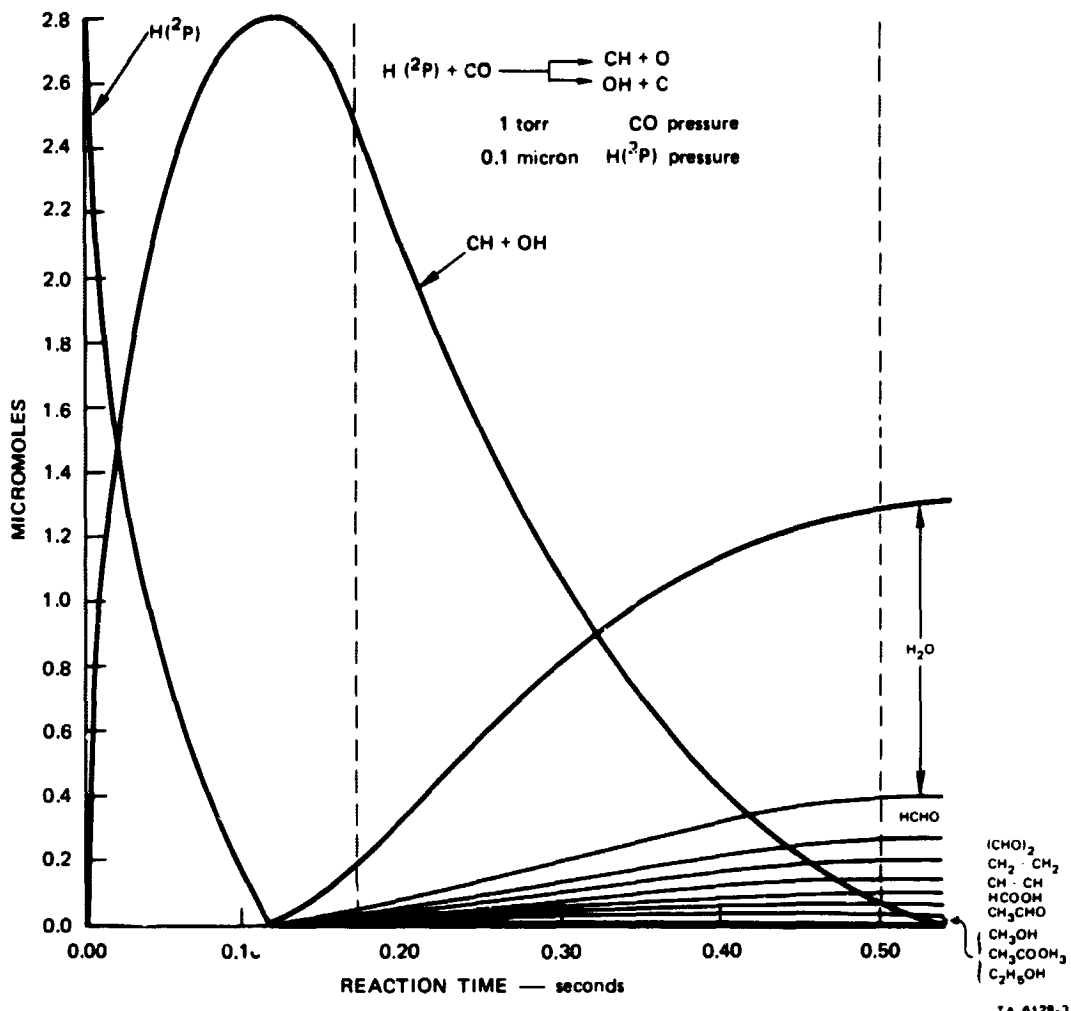


FIGURE 2 LIFETIME OF REACTANTS AND FORMATION RATES OF PRODUCTS

After system calibration with several compounds, a number of runs were made using a hydrogen irradiation lamp containing a flowing mixture of 10% H<sub>2</sub> in He at a pressure of a few torr. The following combinations of CO<sub>2</sub> and CO were used in a series of reaction experiments with hydrogen:

- (1) 100% CO
- (2) 0.1% CO<sub>2</sub> in CO
- (3) 10% CO<sub>2</sub> in CO
- (4) 10% CO in CO<sub>2</sub>
- (5) 0.1% CO in CO<sub>2</sub>
- (6) 100% CO<sub>2</sub>

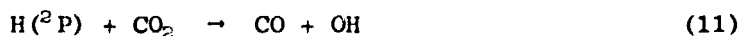
These gases were reacted with hydrogen by passing either the hydrogen or the CO/CO<sub>2</sub> through a microwave cavity for excitation before mixing. The mixture was irradiated by the hydrogen lamp. Carbon dioxide dissociated into excited CO and H<sub>2</sub> at a total pressure of 2 torr react to form water and organic compounds.

The next series of experiments was made, using the following conditions. A mixture of 0.1% H<sub>2</sub> in CO<sub>2</sub> was prepared and this mixture passed through the gas reaction system at a total pressure of 1 torr (one micron H<sub>2</sub> partial pressure). This mixture was used with three variations: microwave cavity excitation only, hydrogen lamp irradiation only, and excitation plus irradiation. No detectable organic compounds were produced under any of these conditions.

The above experiment was repeated using 10% H<sub>2</sub> in CO<sub>2</sub> (pressure 1 torr; excitation only, irradiation only, and both) and again no organic compounds were formed.

Based on what is now known about the Venus atmosphere, the experiments in which the CO<sub>2</sub> and H<sub>2</sub> were mixed and passed through the microwave discharge probably gave the closest approximation to conditions in the

dissociation region. With some H<sub>2</sub> dissociation and excitation the following reactions occur:



Reactions (11) and (14) combined are

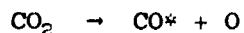


and the net result is no carbon hydrogen bond formation, only changes of oxidation state.

The gas mixture was then changed to 75% H<sub>2</sub> and 25% CO introduced separately into the irradiation chamber at a total pressure of 1.3 torr. This combination produced very large amounts of organics when either gas was excited prior to mixing, with or without Lyman- $\alpha$  irradiation.

When pure CO was passed through the microwave cavity, large amounts of carbon were deposited on the walls of the tubing. To avoid carbon deposition, this experiment was repeated using hydrogen lamp irradiation only. No organics were produced under these conditions.

The characteristics of the reaction series beginning with CO<sub>2</sub> dissociation in a microwave discharge



then adding H<sub>2</sub> downstream of the excitation point



were studied to determine the kinds of stable products formed and their amounts. A large number of experimental runs were made using one torr of CO<sub>2</sub> and 100 microns of H<sub>2</sub>. These conditions were selected as the best probable laboratory analog to the high Venus atmosphere. Reaction products

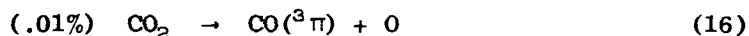


were collected, first without the hot CaC<sub>2</sub> cartridge ahead of the flame ionization detector, and the CaC<sub>2</sub> cartridge was then placed in the system to determine the amount of water produced. Finally experiments were made in which the reacting mixture was irradiated with the hydrogen lamp to determine the effect of irradiation on product yield.

The relatively high pressures used, and the presence of surfaces in the reaction studies cause a large difference between the conditions of investigation and the probable conditions of reaction in the high atmosphere of Venus.

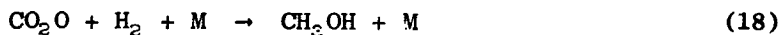
In all of the experiments starting with the passage of CO<sub>2</sub> through a microwave discharge, followed by H<sub>2</sub> addition and mixing downstream the reaction produced mainly methanol, 10 to 20 mole % water, and small amounts (1 - 2 mole %) of formaldehyde, glyoxal, acetaldehyde, and ethanol.

When the CO<sub>2</sub> was passed through the microwave discharge, it was completely dissociated into CO and O and about .01% of the CO molecules were excited.



From the laboratory data it was possible to produce a detailed reaction model and mechanism for the conditions used.

The predominant reaction course was:



The other important reaction course was:



The CH radical produced in (19), reacting with other radical species present gave rise to the new products; HCHO, (CHO)<sub>2</sub>, CH<sub>3</sub>CHO, and C<sub>2</sub>H<sub>5</sub>OH in termolecular reactions.

When 1 torr of CO<sub>2</sub> and 0.1 torr of H<sub>2</sub> were used (20 ml/mm CO<sub>2</sub> STP, 2 ml/mm H<sub>2</sub> STP) 0.2 μ moles of methanol, 0.06 μ moles of water and < 0.01 μ moles of other products, all organic, were produced.

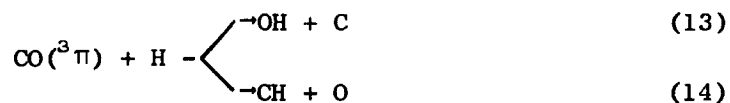
Secondary irradiation of the products with a hydrogen lamp photolyzed one third of the water initially formed and caused an increase in the methanol yield, probably by increasing the rate of the termolecular CH<sub>3</sub>OH producing reactions relative to the bimolecular H<sub>2</sub>O producing reactions.

## CONCLUSIONS

The dissociation level in the Venus atmosphere is believed to be a few kilometers above the cloud tops and, at this level in the predominantly CO<sub>2</sub> atmosphere observed, a large fraction of the water vapor present must be photodissociated. Most of this water is dissociated into H and OH, less than one quarter of it dissociating into H<sub>2</sub> and O.<sup>13</sup> The observed equilibrium concentration of CO<sup>11</sup> is about three times the OH concentration and the most important reaction in this region is then



If a significant fraction of the H atoms produced were excited, some detectable production of carbon-hydrogen bonds would be expected. If a significant fraction of the CO molecules were excited; the reactions



(14)

are not energetically favorable at 220°K and significant carbon-hydrogen bond formation would not be expected. Only if there were a large excess of H<sub>2</sub> would any organic producing reaction involving excited CO be anticipated. Such a condition would produce methane and water only, according to our findings.

As no hydrocarbon or organic molecules have ever been detected in the Venus atmosphere, it must be presumed that there is no significant concentration of H(<sup>2</sup>P) present.

Despite the temperature-water vapor pressure enigma at the cloud top level,<sup>14</sup> which remains unsolved, the most likely composition of the Venus clouds is ice.

## CONTRIBUTORS

Persons who made direct contributions to this project were  
Leonard Cavanagh, Dr. Cecile Naar, Louis Salas, and Conrad Schadt.

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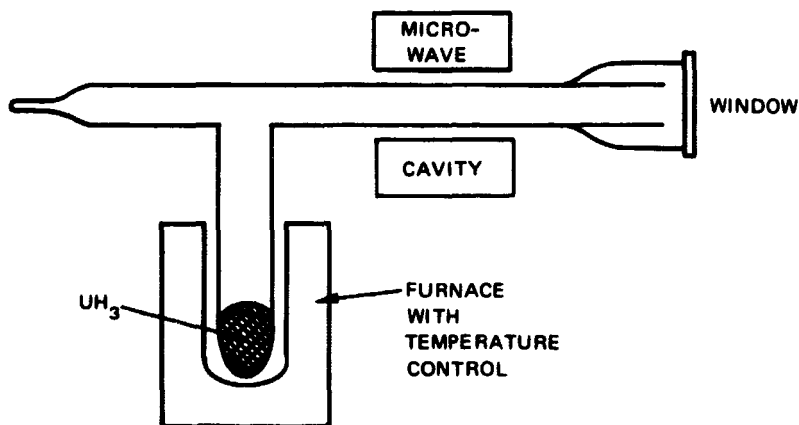
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## Appendix A

### PROCEDURE FOR MAKING URANIUM HYDRIDE HYDROGEN LAMP

A simple high intensity hydrogen lamp can be made by sealing  $\text{UH}_3$  in a Pyrex tube with a LiF window. The simplicity of the lamp is shown in the following figure.



TA-6128-4

FIGURE A-1 URANIUM HYDRIDE HYDROGEN LAMP

To operate this lamp, the  $\text{UH}_3$  is heated to about  $175^\circ$  to dissociate enough  $\text{UH}_3$  to produce a hydrogen pressure of about 3 torr. The hydrogen is excited in a 2450 Mc microwave cavity with a power setting of 100 ma. The Pyrex tube in the cavity must be air cooled, or this part of the lamp can be made of quartz if it is not cooled. The dissociated hot uranium is a very efficient scavenger, combining with all foreign reactive gases and maintaining a very pure hydrogen atmosphere.



The stepwise procedure for making the lamp is as follows:

1. Cement LiF window on lamp.
2. Wash uranium powder in 25% nitric acid solution. Uranium powder will swell to about twice the original volume. Dry uranium with absolute ethanol.
3. Place uranium in finger in lamp and seal lamp in vacuum system. Pump down as fast as possible.
4. Pump for one day with diffusion pump. Check for leaks with Tesla coil.
5. Admit 0.5 atm of  $H_2$ ; exhaust and flush lamp several times.
6. Admit about 0.1 to 0.2 atm of  $H_2$ ; heat uranium to very dull red glow (as viewed in darkness). Be careful not to collapse glass; pump down.
7. Refill with  $H_2$  to 1/2 atm. Heat to dull red glow and pump down again, repeat 3 to 6 times. Uranium should be black. Repeat twice after uranium turns black. If it doesn't turn black after six times, start again.
8. Heat uranium tube finger with furnace--200 to 250°C--overnight.
9. Cool to room temperature.
10. Pump off excess  $H_2$  while cold.
11. Heat to 400°C and hold for 2 hours or longer.
12. Pump off one-half the  $H_2$  left while finger is at 400°C.
13. Cool to room temperature.
14. Seal off. Lamp is ready for use.

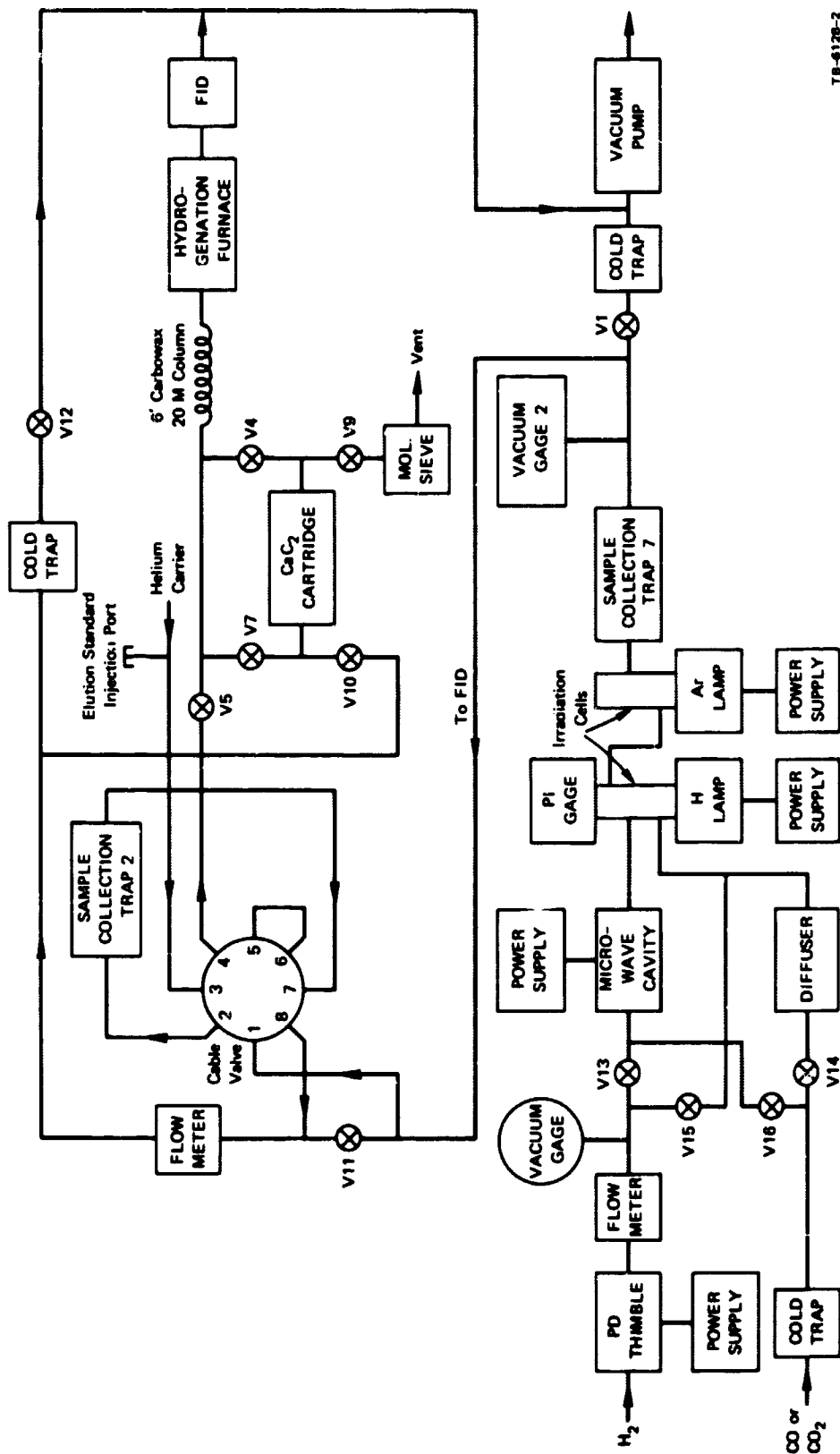
## Appendix B

### EQUIPMENT FOR GAS ANALYSIS

Two systems based on gas chromatography were designed and fabricated in attempts to provide for rapid, high sensitivity analysis of condensed products of the gas phase reactions of interest. A cross-section detector was used in the first of these systems in an attempt to detect water, carbon suboxide, formaldehyde, formic acid, etc.

Although the major reaction products were measurable (three or four components) using the cross-section detector, the minor components were obscured by background noise. Reaction runs longer than 30 minutes to permit generation of larger quantities of reaction products were not practical. Hydrogen gas from the reaction system was used as the carrier gas and during chromatography the hydrogen pressure was increased to greater than a half-atmosphere to obtain the best possible sensitivity with the cross-section detector. This pressurization step was slow as the maximum flow of  $H_2$  through the palladium thimble was limited to about 20 ml/mm STP (overall system volume was 700 ml). The cross-section detector required a very stable flow of  $H_2$  and it was found that it could not be satisfactorily stabilized in this kind of system; also its sensitivity was not good enough to meet our requirements. So we substituted the flame-ionization detector (FID) for the cross-section detector, adding a hydrogenation furnace for the detection of HCHO, HCOOH, and  $C_2O$ , and a  $CaC_2$  cartridge for the detection of water.

The entire reaction-analysis system as finally designed, with FID + hydrogenation furnace +  $CaC_2$  cartridge, is shown in the flow diagram, Fig. B-1.



TB-6126-2

FIGURE B-1 FLOW DIAGRAM OF GAS REACTION-ANALYSIS APPARATUS

The operating procedure for sample transfer and analysis is outlined in the following section.

#### Transfer of Collected Sample

At the end of reaction periods,  $V_{14}$  was closed,  $V_1$  was closed, and  $V_{13}$  opened full. Power to Pd thimble was increased to maximum and system  $H_2$  pressure then increased to about 100 torr. At this  $H_2$  pressure,  $V_{12}$  and  $V_5$  were opened;  $V_1$ ,  $V_{11}$ ,  $V_7$ ,  $V_4$ ,  $V_9$ ,  $V_2$ , and  $V_{10}$  were closed. Sample collection trap No. 2 was  $LN_2$  cooled. Cold finger No. 1 collant ( $LN_2$ ) was removed, 1 minute warm up was allowed, then immersed in  $95^\circ C$  water. Transfer time was 15 minutes.

#### Measurement of Organics

$V_{11}$ ,  $V_4$ ,  $V_{10}$ ,  $V_5$ ,  $V_7$ ,  $V_2$ ,  $V_9$ ,  $V_1$ , and  $V_{12}$  were closed and  $V_5$  was opened. Sample collection trap No. 2 collant was removed: 1-1/2 minute warm up, then  $95^\circ C$  water chromatographic column and detected by FID.

Water measurements are made by shunting the sample through  $CaC_2$  furnace. To shunt the sample through  $CaC_2$  furnace, all above valve positions were the same, except  $V_5$  was closed and  $V_4$  and  $V_7$  were open. This permits the collected organics to be routed through the  $CaC_2$  cartridge and the water in the sample reacts with  $CaC_2$  to produce acetylene. Valves  $V_{10}$  and  $V_9$  permit the hot ( $165^\circ C$ )  $CaC_2$  cartridges to be evacuated and flushed with dry air to remove any residual  $HC\equiv CH$  that accumulated during extended intervals of isolation from the rest of the system.

A Carle Model 2012 valve was installed in the detection system, providing a convenient means of isolating the analytical system from the vacuum system, as the FID must be operated at ambient pressure. During sample transfer from sample collection trap No. 1 to sample collection trap No. 2, the Carle valve was in the counterclockwise position.

Valves  $V_1$ ,  $V_{11}$ ,  $V_7$ ,  $V_{10}$ ,  $V_9$ , and  $V_4$  are closed;  $V_5$  and  $V_{12}$  were open at initiation of transfer. The reaction products plus the transfer hydrogen carrier pass into port 1 out of port 2 and into the sample collection trap. The sample collection trap was packed with 20% Carbowax 20M on 60/80 mesh Chromosorb W. The reaction products were trapped and the transfer carrier hydrogen passed into port 7 out of port 8 through  $V_{12}$  to the vacuum pump. In this valve position helium carrier gas passes in port 3 and out port 4 through column, hydrogenation furnace, and into the FID continuously. At the end of the transfer period the Carle valve is moved to the clockwise position. The collection trap is valved out of the vacuum system and into the helium carrier gas line associated with the FID. The helium carrier enters port 3, out port 2, through the collection trap, in port 7, out port 6, in port 5, out port 4, through  $V_5$ , through the separation column (through the hydrogenation furnace, if desired), and into the FID.

#### Advantages of FID System Over Cross-Section System

1. The FID is approximately  $10^3$  more sensitive than the cross-section detector, hence minor reaction products can be measured with precision.
2. The FID is not sensitive to changes in carrier flow and permits a more efficiently packed collection trap to be used.
3. The transfer can be accomplished at lower pressures through reducing the time required to pressurize with hydrogen.
4. This modification permits elution standards to be injected only into the collection trap instead of the entire generation system as with the cross-section detector.